



AFRL-RY-WP-TR-2017-0193

METASTABLE POLYMERS FOR ON-DEMAND TRANSIENT ELECTRONIC PACKAGING

Jeffrey Moore, John Rogers, Nancy Sottos, and Scott White
University of Illinois Champaign

JANUARY 2018
Final Report

Approved for public release; distribution is unlimited.

See additional restrictions described on inside pages

STINFO COPY

AIR FORCE RESEARCH LABORATORY
SENSORS DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7320
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE

NOTICE AND SIGNATURE PAGE

Using Government drawings, specifications, or other data included in this document for any purpose other than Government procurement does not in any way obligate the U.S. Government. The fact that the Government formulated or supplied the drawings, specifications, or other data does not license the holder or any other person or corporation; or convey any rights or permission to manufacture, use, or sell any patented invention that may relate to them.

This report is the result of contracted fundamental research deemed exempt from public affairs security and policy review in accordance with SAF/AQR memorandum dated 10 Dec 08 and AFRL/CA policy clarification memorandum dated 16 Jan 09. This report is available to the general public, including foreign nationals.

Copies may be obtained from the Defense Technical Information Center (DTIC)
(<http://www.dtic.mil>).

AFRL-RY-WP-TR-2017-0193 HAS BEEN REVIEWED AND IS APPROVED FOR
PUBLICATION IN ACCORDANCE WITH ASSIGNED DISTRIBUTION STATEMENT.

// Signature//

STEPHEN E. TETLAK, Program Manager
Devices for Sensing Branch
Aerospace Components & Subsystems Division

// Signature//

ROSS W. DETTMER, Chief
Devices for Sensing Branch
Aerospace Components & Subsystems Division

// Signature//

JAMES M. SATTler, Lt Col, USAF
Deputy
Aerospace Components & Subsystems Division
Sensors Directorate

This report is published in the interest of scientific and technical information exchange, and its publication does not constitute the Government's approval or disapproval of its ideas or findings.

*Disseminated copies will show “//Signature//” stamped or typed above the signature blocks.

REPORT DOCUMENTATION PAGE				<i>Form Approved</i> OMB No. 0704-0188	
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YY) January 2018		2. REPORT TYPE Final		3. DATES COVERED (From - To) 23 March 2015 – 27 August 2017	
4. TITLE AND SUBTITLE METASTABLE POLYMERS FOR ON-DEMAND TRANSIENT ELECTRONIC PACKAGING				5a. CONTRACT NUMBER FA8650-15-C-7522	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 61101E/62716E	
6. AUTHOR(S) Jeffrey Moore, John Rogers, Nancy Sottos, and Scott White				5d. PROJECT NUMBER 1000	
				5e. TASK NUMBER N/A	
				5f. WORK UNIT NUMBER Y18K	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Illinois Champaign 506 S. Wright St, 364 Henry Admin Bldg Urbana, IL 61801-3620				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory Sensors Directorate Wright-Patterson Air Force Base, OH 45433-7320 Air Force Materiel Command United States Air Force				10. SPONSORING/MONITORING AGENCY ACRONYM(S) AFRL/RYYD	
				11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S) AFRL-RY-WP-TR-2017-0193	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES This report is the result of contracted fundamental research deemed exempt from public affairs security and policy review in accordance with SAF/AQR memorandum dated 10 Dec 08 and AFRL/CA policy clarification memorandum dated 16 Jan 09. This material is based on research sponsored by Air Force Research laboratory (AFRL) and the Defense Advanced Research Agency (DARPA) under agreement number FA8650-15-C-7522. The U.S. Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation herein. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies of endorsements, either expressed or implied, of AFRL and the DARPA or the U.S. Government. Report contains color.					
14. ABSTRACT The thermally-triggered depolymerization of cyclic poly(phthalaldehyde) (cPPA) was investigated and tailored to enable thermal processing and molding in bulk quantities. Stabilization of cPPA at elevated temperature was accomplished by removal of the latent Lewis acid catalyst BF ₃ and by addition of radical inhibitors and a Lewis base. Addition of a plasticizer to the stabilized cPPA enabled the fabrication of a monolithic solid polymer via hot press molding. The bulk material retains the transient properties of cPPA when triggered by sufficient heat or acid.					
15. SUBJECT TERMS depolymerization, poly(phthalaldehyde), microcooler, thermal					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT: SAR	18. NUMBER OF PAGES 32	19a. NAME OF RESPONSIBLE PERSON (Monitor) Stephen Tetlak 19b. TELEPHONE NUMBER (Include Area Code) N/A
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			

Table of Contents

Section	Page
List of Figures	ii
List of Tables	ii
1 SUMMARY	1
2 INTRODUCTION	2
2.1 Background	2
2.2 Approach	3
3 METHODS, ASSUMPTIONS, AND PROCEDURES	4
3.1 Materials and Instrumentation	4
3.2 Solvent Casting cPPA Films	4
3.2.1 Pristine cPPA Films	4
3.2.2 Inhibited cPPA Films	5
3.2.3 cPPA Film for Hot Pressing Feedstock	5
3.3 Purification of cPPA	5
3.4 Comparative Properties of S-cPPA and P-cPPA	6
3.4.1 GPC Analysis of S-cPPA and P-cPPA	6
3.4.2 ¹ H NMR Analysis of S-cPPA and P-cPPA	6
3.4.3 Impurity Calculations for S-cPPA and P-cPPA	7
3.5 Thermal Processing of cPPA	8
3.6 Triggered Depolymerization of Bulk cPPA	10
3.6.1 Acid-Catalyzed Degradation	10
3.6.2 Thermal Degradation	10
4 RESULTS AND DISCUSSION	11
4.1 Stabilization of cPPA by Additives	11
4.2 Stabilization of cPPA by Purification	11
4.3 Bulk Processing of cPPA	14
4.3.1 Plasticization of cPPA	14
4.3.2 Thermoforming Bulk cPPA	15
4.3.3 Transient Properties of Bulk cPPA	16
4.4 Previous Research Directions and Publications	16
4.4.1 Ultraviolet-Triggered Transient Electronics	17
4.4.2 Thermally-Triggered Acid-Wax Emulsions for Transient Electronics	18
4.4.3 Thermally-Triggered Poly(vinyl <i>t</i> -butyl carbonate sulfone) Acid Generators and Their Use in the Depolymerizations of cPPA	18
4.4.4 Poly(olefin sulfone)s	19
4.4.5 Unproductive Research Directions	20
4.4.5.1 Mechanically Robust Base-Sensitive Polymers	20
4.4.5.2 Flash-Triggering by Acid Amplification	20
4.4.5.3 Frontal Depolymerization	20
4.5 Commercialization of cPPA	21
4.5.1 Molecular Properties	22
4.5.2 Stability and Utility in Transient Materials Applications	23
5 CONCLUSIONS	24
6 REFERENCES	25
LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS	26

List of Figures

Figure	Page
Figure 1: Previously Proposed cPPA Degradation Mechanisms	3
Figure 2: GPC Comparison of S-cPPA and P-cPPA	6
Figure 3: NMR Comparison of S-cPPA and P-cPPA	7
Figure 4: Schematic of cPPA Hot Pressing Procedure	9
Figure 5: Validation of cPPA Integrity after Hot-Press Molding	9
Figure 6: ¹ H NMR of cPPA Bulk Solid in THF-d ₈ before (top) and after (bottom) Exposure to Trifluoroacetic Acid.....	10
Figure 7: Effects of TEMPO and DBPDA on cPPA Thermal Stability	11
Figure 8: Effects of Impurities and Stabilizers on cPPA Thermal Stability	13
Figure 9: Thermal Transitions of Plasticized cPPA.....	15
Figure 10: Thermal Processing of cPPA.....	15
Figure 11: Demonstrated Transience of Monolithic cPPA.....	16
Figure 12: Frontal Depolymerization of a Locally Depolymerized Neat cPPA film at 105°C ...	21
Figure 13: GPC Analysis of cPPA Obtained from Sigma Aldrich.....	22
Figure 14: NMR Analysis of cPPA Obtained from Sigma Aldrich.....	22

List of Tables

Table	Page
Table 1. Representative Molecular Weight Data for S-cPPA and P-cPPA	6
Table 2. Fluorine and BF ₃ Concentrations as Determined by Elemental Analysis for S-cPPA and P-cPPA	7
Table 3. ¹ H NMR Integrations for cPPA and Methanol in THF-d ₈ and Calculated Residual Methanol Concentration.....	8
Table 4. GPC Molecular Weight Data for P-cPPA Feedstock and Bulk cPPA.....	9
Table 5. Concentrations of Methanol and BF ₃ , and Molecular Weight Data for S-cPPA and P-cPPA	12

1 SUMMARY

The thermally-triggered depolymerization of cyclic poly(phthalaldehyde) (cPPA) was investigated and tailored to enable thermal processing and molding in bulk quantities. Stabilization of cPPA at elevated temperature was accomplished by removal of the latent Lewis acid catalyst boron trifluoride (BF_3) and by addition of radical inhibitors and a Lewis base. Addition of a plasticizer to the stabilized cPPA enabled the fabrication of a monolithic solid polymer via hot press molding. The bulk material retains the transient properties of cPPA when triggered by sufficient heat or acid.

2 INTRODUCTION

2.1 Background

Since its first description in 1969^{1,2}, poly(phthalaldehyde) (PPA) has garnered extensive interest due to its rapid depolymerization in response to stimuli such as acid^{1,3-7}, moderate heat^{8,9}, and mechanochemical activation¹⁰. PPA depolymerizes rapidly because it has a low ceiling temperature of -42°C ², meaning that it is thermodynamically unstable at ambient conditions. Cleavage of the polymer backbone or end group removes the kinetic stability of the polymer and initiates a very rapid chain unzipping process into the monomer, *ortho*-phthalaldehyde (*o*PA). In the 1980s PPA was primarily investigated for use in lithographic processes,^{4,11} and more recently has been considered as an attractive candidate for a broad range of transient materials, i.e., stimuli-responsive materials that undergo rapid depolymerization in response to a triggering event.^{3,9} Toward this end, multiple studies have described the tailoring of materials properties via telechelic functionalization¹², end-group functionalization^{13,14}, pendent group modifications,^{15,16} or copolymerization^{12,17}. In 2013 we reported that the high-yielding, high molecular weight preparation of PPA by Lewis acid catalysis results in a cyclic polymer (cPPA).⁸ The development of cPPA presented a significant materials opportunity, given a more facile synthesis^{8,14} and improved mechanical properties compared to its linear counterpart, while maintaining its innate transient functionality.

The transient nature of the polymer poses two distinct challenges in application. First, the stability and thermal degradation behavior of cPPA varies wildly. Even within a single batch¹⁸, a range of temperature onsets of depolymerization have been reported, with instances of spontaneous depolymerization under ambient conditions. This unpredictability precludes standardization, and hence impacts the reliability of these materials for transient applications. Second, bulk materials and monolithic form factors based on cPPA remain elusive, with applications and studies of cPPA relegated to those of powders or solvent-cast thin films.^{3-5,8-10,13,15} The relatively low degradation temperature of cPPA (ca. 100°C) precludes thermal processing, as the polymer degrades before any thermal transition, with an estimated T_g of ca. 180°C .¹⁷

Understanding the degradation behavior of cPPA is complicated by the fact that differing degradation mechanisms have been proposed in multiple reports. Computational and experimental studies have suggested both a homolytic, radical chain unzipping mechanism during thermolysis¹⁸, and a cationic, acid-catalyzed unzipping mechanism¹⁹. The two proposed mechanistic pathways are shown in Figure 1. Given competing possible reaction pathways, and that multiple experimental and processing parameters could conceivably impact the observed degradation behavior derived from either of the potential degradation mechanisms, it is perhaps unsurprising that the thermal degradation behavior of cPPA is unpredictable.

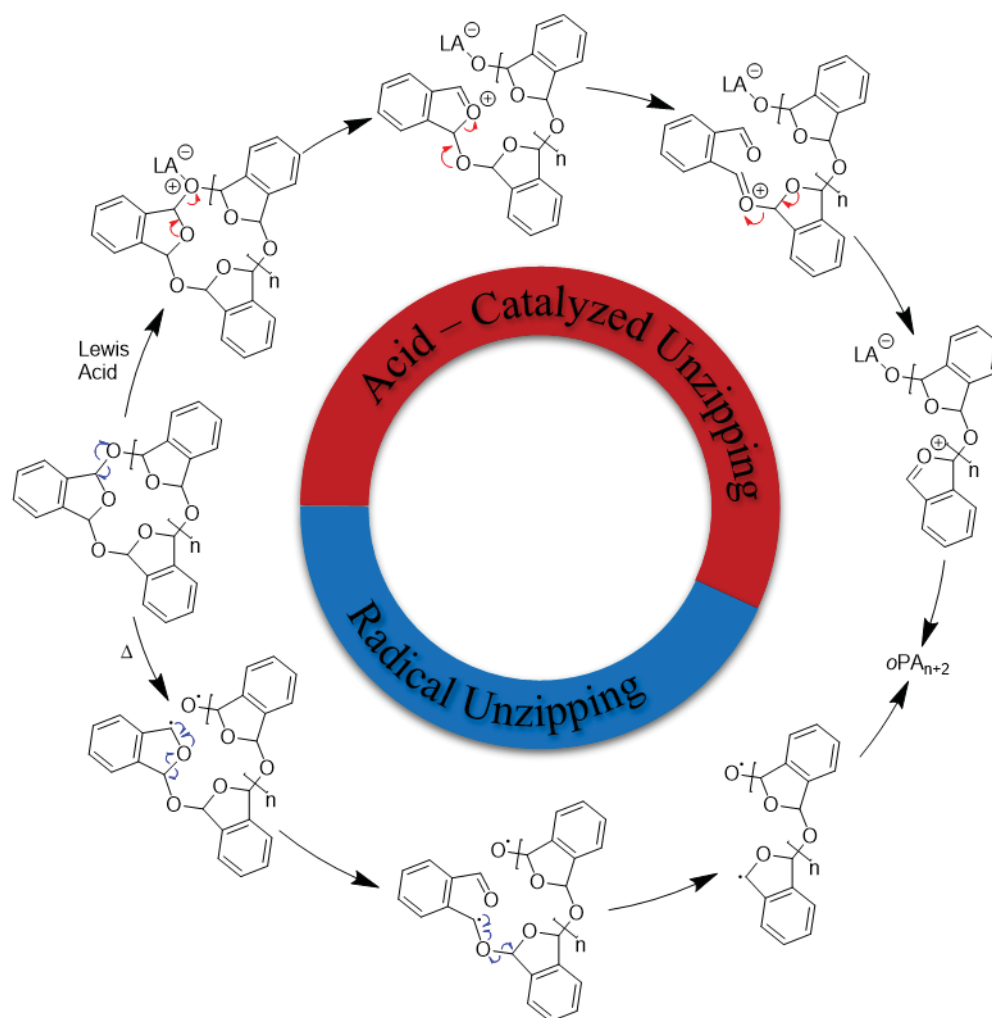


Figure 1: Previously Proposed cPPA Degradation Mechanisms
Acid-catalyzed, cationic unzipping (top, red) and homolytic, radical chain unzipping (bottom, blue).

2.2 Approach

This research aimed to use the previously proposed depolymerization mechanisms of cPPA as a theoretical scaffold from which to modify the thermal stability of cPPA. The effects of radical inhibitor and Lewis base additives, as well as trace synthetic impurities, are investigated. The improvements we report in thermal stability of the polymer are leveraged to thermally process plasticized cPPA into a bulk solid. Finally, we demonstrate that the transient properties of the bulk solid are preserved.

3 METHODS, ASSUMPTIONS, AND PROCEDURES

3.1 Materials and Instrumentation

Unless otherwise specified, all materials were purchased from Sigma-Aldrich and used without further purification. High-performance liquid chromatography (HPLC) grade solvents were purchased from commercial sources and used without further purification for polymer purification and solvent casting. HPLC grade methanol was purchased from VWR, and HPLC grade dichloromethane was purchased from Fisher Scientific. *ortho*-Phthalaldehyde was purchased from TCI America and purified by recrystallization, according to a literature procedure.⁸ Cyclic poly(phthalaldehyde) was synthesized via a previously reported procedure.⁸

Analytical gel permeation chromatography (GPC) was performed using a Waters 1515 isocratic HPLC pump and Waters 2707 96-well autosampler, equipped with a Waters 2414 refractive index detector and 4 Waters HR Styragel columns (7.8×300 mm, HR1, HR3, HR4, and HR5) in tetrahydrofuran (THF) at 30°C. The GPC system was calibrated using monodisperse polystyrene standards.

Dynamic thermogravimetric analysis (TGA) was performed using a TA Instruments Q500 TGA under a nitrogen atmosphere (90 mL/min). Dynamic TGA traces were obtained during a 5°C/min ramp after equilibration at 45°C. TGA samples consisted of 5-6 mg of the analyte film in a platinum pan.

¹Hydrogen (H) nuclear magnetic resonance (NMR) spectra were recorded at 500 MHz using a Bruker Ascend 500 spectrometer equipped with a 5 mm broadband cryoprobe and SampleXpress autosampler. Spectra were obtained in either chloroform-*d* or tetrahydrofuran-*d*₈. Residual proton solvent was used as an internal standard (CHDCl₂ (1 H) 5.32 ppm; THF-*d*₇ (1 H), 1.72 and 5.32 ppm).

Dynamic mechanical analysis (DMA) was performed on a TA Instruments RSA III fitted with thin film grips provided by TA Instruments. Specimen dimensions were 5 mm \times 20 mm \times 200 μ m, and the gauge length was set to 10 mm. Dynamic loading was applied at 1 Hz and 0.1 % strain amplitude, and the temperature was increased 5°C/min from -60 to 80°C.

Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q20 differential scanning calorimeter. Polymer samples weighing ca. 5 mg were loaded into a standard aluminum pan and sealed with a hermetic lid. The samples were cooled to -100°C and ramped at 20°C/min to 115°C, and the cooling/heating cycle was repeated for a total of three heating cycles.

3.2 Solvent Casting cPPA Films

3.2.1 Pristine cPPA Films

cPPA films were prepared using a modification of a literature procedure.^{3,9} For example: cPPA (100 mg) was dissolved in HPLC grade dichloromethane (3 mL), and gently vortexed until the mixture was no longer turbid. The solution was then cast into a 50 mm diameter

poly(tetrafluoroethylene) (PTFE)-lined petri dish and placed in an enclosure with an atmosphere partially saturated with dichloromethane. The film was allowed to dry undisturbed at 22°C for 24 h, affording a free-standing 95 mg film. After drying, the film was stored at -20°C until use.

3.2.2 Inhibited cPPA Films

Inhibited cPPA films were produced by modification of the same method described above. For example: 10.0 mg of TEMPO was dissolved in 5.0 mL of HPLC grade dichloromethane. 100 mg cPPA was weighed into a scintillation vial, and 1.0 mL of the (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) solution was added, followed by 2.0 mL of HPLC grade dichloromethane (DCM). The solution was then cast into a 50 mm diameter PTFE-lined petri dish and placed in an enclosure with an atmosphere partially saturated with dichloromethane. The film was allowed to dry undisturbed at 22°C for 24 h, affording an orange, free-standing 98 mg film. After drying, the film was stored at -20°C until use.

3.2.3 cPPA Film for Hot Pressing Feedstock

A modification of the above procedure was used to produce the cPPA film used as feedstock for hot pressing. Briefly, 1600 mg of cPPA was weighed into a 50 Erlenmeyer flask and dissolved into 15 mL HPLC grade DCM. *N,N'*-di-*sec*-butyl-1,4-phenylenediamine (DBPDA) (48 mg) and diethylphthalate (DEP) (320 mg) were weighed into a scintillation vial and dissolved in 5 mL dichloromethane. The DBPDA/DEP solution was then added to the cPPA solution, and the mixture was vortexed briefly to ensure thorough mixing. The solution was then cast into a 100 mm diameter PTFE-lined petri dish and placed in an enclosure with an atmosphere partially saturated with dichloromethane. The film was allowed to dry undisturbed at 22°C for 24 h, and subsequently dried *in vacuo* for 24 h to ensure thorough removal of residual solvent. A free standing, red orange-red film was obtained (2.0 g) and stored at -20°C until use.

3.3 Purification of cPPA

The purification of cPPA was accomplished by the slow precipitation of the polymer from dichloromethane into methanol. A representative procedure is as follows: cPPA produced via standard protocols, heretofore referred to as standard process cyclic poly(phthalaldehyde) or S-cPPA (5.0 g, $M_n = 231$ kDa) was dissolved in 50 mL HPLC grade DCM. The cPPA solution was then added dropwise via burette to 1.0 L of HPLC grade methanol at an approximate flow rate of 1 mL/min. After dropwise addition was complete, the methanol mixture was decanted, and the polymer was immersed in 100 mL of methanol. After settling for 30 min, the methanol-polymer mixture was decanted again. Immersion in another 100 mL of methanol, followed by suction filtrated afforded a white solid. The polymer was dried *in vacuo* for 24 h, and the purified cPPA (P-cPPA) was recovered as a brittle white solid (3.5 g, M_n 266 kDa).

3.4 Comparative Properties of S-cPPA and P-cPPA

3.4.1 GPC Analysis of S-cPPA and P-cPPA

To confirm that the purification of cPPA resulted in a polymer with similar molecular weight characteristics, GPC traces of S-cPPA and P-cPPA produced from the same batch of polymer were analyzed (Figure 2). The molecular weight data for the two polymers is summarized in Table 1. The M_n increases slightly upon purification of cPPA, while the M_w remains largely unchanged, resulting in a more monodisperse polymer after purification. This is likely the result of small molecules and oligomers being removed during the purification process.

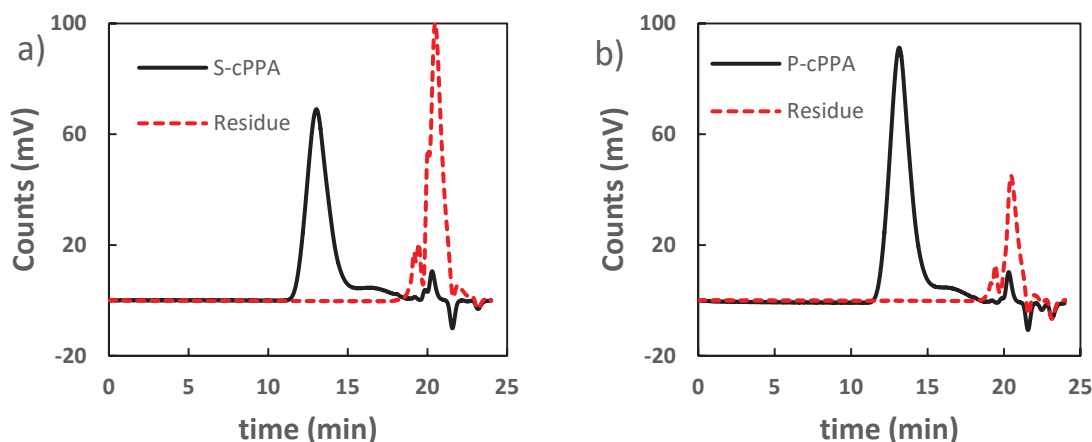


Figure 2: GPC Comparison of S-cPPA and P-cPPA

Representative GPC traces of (a) S-cPPA and (b) P-cPPA powder before and after degradation triggered by heating to 140°C for 5 minutes.

Additionally, samples of S-cPPA and P-cPPA were heated to 140°C in an oven for 5 minutes. The polymers degraded rapidly, leaving behind a visible residue. GPC analysis of the residue (Figure 2) indicates that both S-cPPA and P-cPPA undergo rapid thermal degradation, generating exclusively small molecule products.

Table 1. Representative Molecular Weight Data for S-cPPA and P-cPPA

Polymer	M_n (kDa)	M_w (kDa)	Polydispersity Index (PDI)
S-cPPA	231	330	1.42
P-cPPA	266	329	1.23

3.4.2 ^1H NMR Analysis of S-cPPA and P-cPPA

In addition to analysis by GPC, the S-cPPA and P-cPPA were analyzed by ^1H NMR (Figure 3). The spectra of the polymer samples match those reported previously.⁸ Additionally, when samples of S-cPPA and P-cPPA were heated to 140°C for five minutes, the polymers degraded rapidly, leaving behind a visible residue. ^1H NMR analysis of the residue from both S- and P-cPPA thermal degradations indicates that both degradations result in the formation of oPA as the primary product.

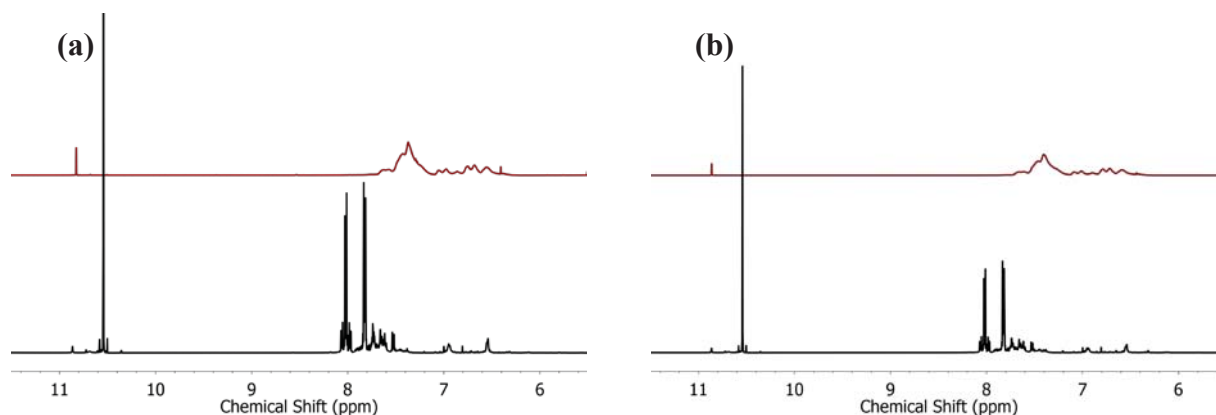


Figure 3: NMR Comparison of S-cPPA and P-cPPA

Representative NMR spectra of (a) S-cPPA and (b) P-cPPA powder before (top, red) and after (bottom, black) degradation triggered by heating to 140°C for 5 minutes. Spectra were collected in THF-*d*₈.

3.4.3 Impurity Calculations for S-cPPA and P-cPPA

The concentration of BF₃ in S-cPPA and P-cPPA was calculated from the mass % of fluorine present in the polymer sample, as measured by elemental analysis. The calculation is as follows:

$$\text{wt}\%_{\text{BF}_3} = \text{wt}\%_{\text{F}} \times \frac{\text{MW}_{\text{BF}_3}}{3 \times \text{MW}_{\text{F}}}$$

$$[\text{BF}_3] = \frac{\text{wt}\%_{\text{BF}_3}}{100 \times \text{MW}_{\text{BF}_3}}$$

Where wt%_{BF₃} is the weight percent of BF₃ in the polymer, wt%_F is the weight percent of fluorine in the polymer, as measured directly by elemental analysis, and MW_x is the molecular weight/atomic mass of the respective moiety. Or, in a simplified version:

$$[\text{BF}_3] = \frac{\text{wt}\%_{\text{F}}}{300 \times \text{MW}_{\text{F}}}$$

Table 2 summarizes the fluorine concentrations measured by elemental analysis and the calculated BF₃ concentrations for S-cPPA and P-cPPA.

Table 2. Fluorine and BF₃ Concentrations as Determined by Elemental Analysis for S-cPPA and P-cPPA

Polymer	[F] (wt. %)	[BF ₃] (μmol/g)
S-cPPA	.10	17.5
P-cPPA	.02	3.5

The concentration of methanol in S-cPPA, P-cPPA and methanol-doped S-cPPA was determined by integration of the methanol methyl proton resonance in THF-*d*₈ at 3.27 ppm. The methyl resonance was compared to the total resonance integration of the cPPA polymer. The calculation is as follows:

$$[\text{MeOH}] = \frac{I_{\text{MeOH}}/H_{\text{MeOH}}}{I_{\text{cPPA}}/H_{\text{cPPA}}} \times \frac{1}{\text{MR}}$$

Where I_{MeOH} is the integral of the methanol methyl resonance and I_{cPPA} is the integral of the cPPA resonance; H_{MeOH} is the number of protons corresponding to the methanol methyl resonance (3), and H_{cPPA} is the number of protons corresponding to the cPPA repeat unit resonance (6); and MR is the molecular weight of the repeat unit (134.14 Da). Table 3 summarizes the integration values measured from the ¹H NMR spectra, as well as the calculated methanol concentrations in S-cPPA, P-cPPA, and methanol-doped S-cPPA.

Table 3. ¹H NMR Integrations for cPPA and Methanol in THF-*d*₈ and Calculated Residual Methanol Concentration

Polymer	I_{MeOH}	I_{cPPA}	[MeOH] (μmol/g)
S-cPPA	11.04	6000	27.4
P-cPPA	19.08	6000	47.3
MeOH-Doped S-cPPA	21.05	6000	52.3

3.5 Thermal Processing of cPPA

Hot pressed cPPA bulk solids were fabricated from the solvent cast films described in Section 3.2.3. The general process for fabrication of cPPA bulk solids is shown schematically in Figure 4. The blended P-cPPA feed stock was cut into ca. 3 mm square shreds, which were then placed into the female half of a circular aluminum mold that was treated with a PTFE mold release agent and preheated to 100°C in an oven. The feed stock was allowed to equilibrate in the oven at 100°C, at which point the male half of the mold was placed on top, and 80 kPa of downward force was applied. After 15 minutes, the mold was removed from the oven and cooled to room temperature while maintaining the 80 kPa compressive force. After cooling, the bulk cPPA disk was removed from the mold. The disk was then cut into ca. 3 mm pellets, which were used as the feed stock for the fabrication of the cPPA triangle. The hot pressing procedure for fabrication of the cPPA triangle was identical to that of the disk.

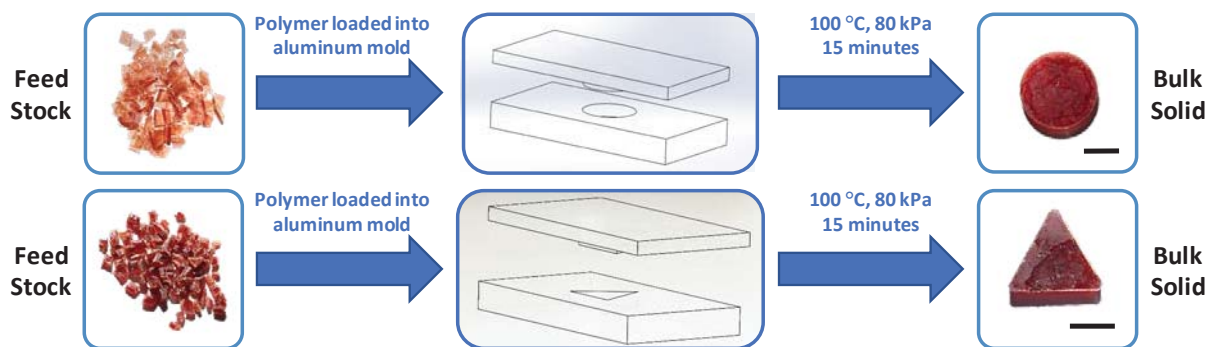


Figure 4: Schematic of cPPA Hot Pressing Procedure
Scale bars are 12.7 mm.

The integrity of the bulk cPPA solid was analyzed by GPC. As shown in Figure 5, the GPC traces of the feed stock and bulk material agree, and show no significant change in molecular weight or distribution. The molecular weight data for the feed stock and bulk polymer are summarized in Table 4. The data indicate that the cPPA blend is stable to thermoforming conditions.

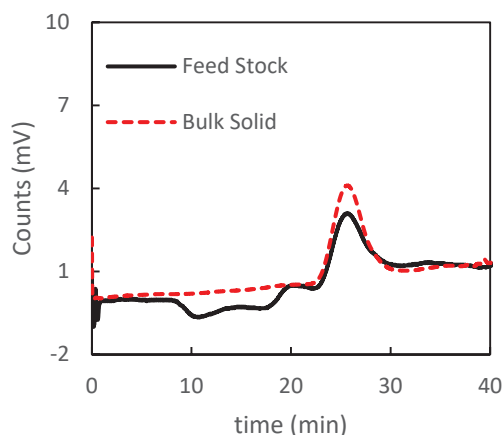


Figure 5: Validation of cPPA Integrity after Hot-Press Molding
GPC traces of the cPPA feed stock used in the hot pressing of cPPA bulk solids and the of the cPPA bulk solid after two cycles of hot pressing.

Table 4. GPC Molecular Weight Data for P-cPPA Feedstock and Bulk cPPA

Polymer Source	M_n (kDa)	M_w (kDa)	PDI
Feedstock	130	204	1.58
Bulk cPPA	136	212	1.56

3.6 Triggered Depolymerization of Bulk cPPA

3.6.1 Acid-Catalyzed Degradation

The acid triggered degradation of bulk cPPA was examined by placing a section of the bulk cPPA triangle (ca. 300 mg) onto a PTFE plate and droppering 50 μ L trifluoroacetic acid onto the top of the cPPA solid. Complete degradation of the solid was observed within 15 minutes of the addition of acid. The degradation of the polymer resulted in a yellow, liquid residue. Figure 6 shows the ^1H NMR spectra of the cPPA bulk solid before and after acid degradation. Before acid treatment, the NMR spectrum shows resonances from cPPA, DEP (the plasticizer) and trace *o*PA. After exposure to trifluoroacetic acid, the cPPA resonances are no longer present, and the NMR spectrum shows only DEP and *o*PA, indicating complete unzipping of the polymer.

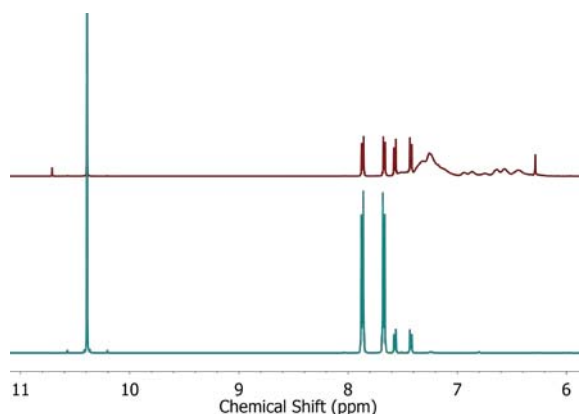


Figure 6: ^1H NMR of cPPA Bulk Solid in THF- d_8 before (top) and after (bottom) Exposure to Trifluoroacetic Acid

3.6.2 Thermal Degradation

The thermal degradation of the bulk cPPA solid was examined by placing a section of the cPPA triangle (ca. 250 mg) onto a glass surface. The surface was then transferred to a hot plate which was preheated to 150°C. The solid rapidly degraded and evaporated, leaving a small amount of a red-black residue. The residue was of insufficient quantity to analyze by GPC or ^1H NMR.

4 RESULTS AND DISCUSSION

4.1 Stabilization of cPPA by Additives

Based on the previously proposed thermal degradation mechanisms of cPPA, two potential degradation inhibitors were chosen for study: TEMPO and DBPDA. TEMPO was expected to act as a radical trap, potentially inhibiting thermal degradation via the previously proposed homolytic unzipping pathway, while DBPDA was expected to behave as a Lewis base, inhibiting degradation in the case of an operative acid-catalyzed degradation pathway.

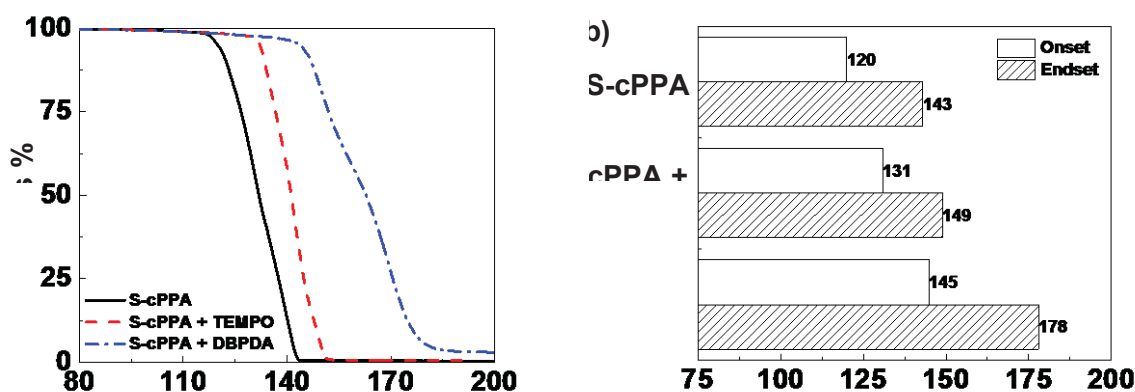


Figure 7: Effects of TEMPO and DBPDA on cPPA Thermal Stability

(a) Dynamic TGA results of S-cPPA films doped with TEMPO and DBPDA during 5°C/min ramp experiments. (b) Bar chart of onset and endset temperatures for neat, TEMPO-doped, and DBPDA-doped S-cPPA films from dynamic TGA experiments.

cPPA thin films were solvent cast from DCM, incorporating 2 parts per hundred rubber (phr) TEMPO and DBPDA, separately, and the thermal degradation was measured by dynamic TGA. These films were cast using cPPA prepared via standard, unoptimized methods (S-cPPA). Interestingly, *both* additives slowed the thermal degradation of cPPA. Representative TGA traces of pristine, TEMPO-doped, and DBPDA-doped cPPA in Figure 7 show significant changes in thermal degradation behavior. Addition of TEMPO increases the average degradation onset temperature from 120°C for the pristine polymer to 131°C, while addition of DBPDA stabilizes the polymer even further, increasing the onset temperature to 145°C. Further, the DBPDA-doped film exhibits the greatest onset-endset gap, indicating that not only does DBPDA increase the onset temperature, but that the degradation kinetics in the presence of DBPDA are significantly slower. Notably, the fact that both TEMPO and DBPDA inhibit thermal degradation of cPPA is consistent with the conclusion that both radical and cationic degradation mechanisms are operative. This suggests that the thermal degradation of cPPA does not follow a single pathway.

4.2 Stabilization of cPPA by Purification

A recent report by the Kohl group suggested that the thermal degradation behavior of cPPA is highly dependent on trace quantities of the polymerization initiator, BF₃.¹⁸ It was reported that treatment of the polymer with triethylamine followed by precipitation into hexanes resulted in

cPPA with increased stability at room temperature, either by sequestration or removal of residual BF_3 . Though changes in the stability at elevated temperature were not reported, the removal of BF_3 was a promising lead to produce cPPA with increased and more consistent thermal stability at elevated temperatures.

In lieu of treatment with triethylamine, it was found that the rate of precipitation of the polymer into methanol greatly impacted the amount of trace BF_3 in the precipitated polymer and, in turn the thermal stability. Typically, cPPA is purified by rapid precipitation from DCM into methanol (S-cPPA).^{3,8} This precipitation affords cPPA with two major impurities- methanol (measured by ^1H NMR) and BF_3 (measured by elemental analysis). Concentrations of methanol and BF_3 for the batch of cPPA used in this study are given in Table 5, though it should be noted that actual concentrations may vary widely. Dropwise precipitation of cPPA from DCM into methanol (ca. 15 μL droplets) resulted in a significantly lower concentration of BF_3 , as well as a higher concentration of methanol (P-cPPA). Additionally, slow precipitation resulted in a slight increase in M_n (231 to 266 kDa) and a decrease in PDI (1.42 to 1.23) due to removal of small molecules and oligomers (Figure 2). It is hypothesized that dropwise precipitation results in greater diffusion of residual BF_3 and oligomer out of the polymer, resulting in a higher purity product.

Table 5. Concentrations of Methanol and BF_3 , and Molecular Weight Data for S-cPPA and P-cPPA

Polymer Sample	Impurity Concentrations		Molecular Weight Data	
	[MeOH] ($\mu\text{mol/g}$)	[BF_3] ($\mu\text{mol/g}$)	M_n (kDa)	PDI
S-cPPA	27.4	17.5	231	1.42
P-cPPA	47.3	3.5	266	1.23

Though the change in the purification process was minor, the observed effects were significant. Dynamic TGA traces of S-cPPA and P-cPPA are shown in Figure 8a. Notably, the improved purification process results in a 26°C increase in the degradation onset temperature. To test the individual effects of methanol and BF_3 , two control experiments were performed. S-cPPA was doped with methanol by adding 5% methanol to the polymer solution in DCM before casting, resulting in a methanol concentration of 50 $\mu\text{L/g}$, similar to that of the purified polymer. While a slight increase in degradation onset and endset temperatures was observed, the small effect does not account for the enhanced stability observed for P-cPPA. Conversely, a P-cPPA film doped with 25 $\mu\text{mol/g}$ BF_3 resulted in significantly depressed onset and endset temperatures, indicating that the presence of BF_3 is extremely detrimental to the thermal stability of the polymer. This suggests that the enhanced stability of the purified cPPA is due to the removal of residual BF_3 .

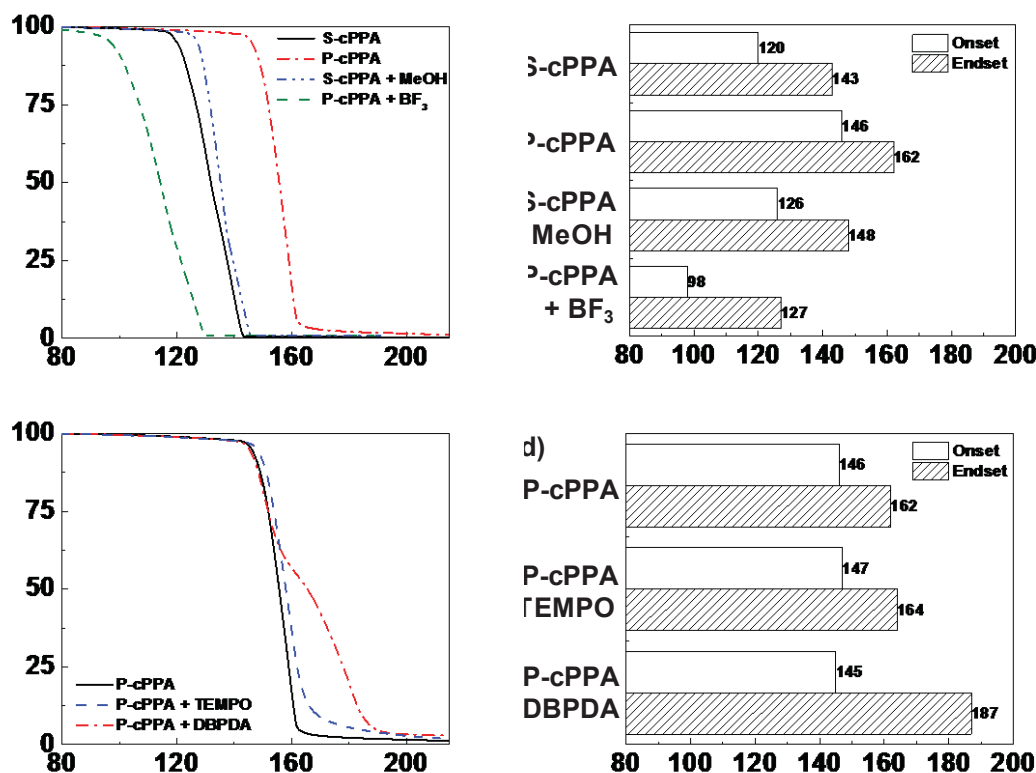


Figure 8: Effects of Impurities and Stabilizers on cPPA Thermal Stability
 (a) Dynamic TGA traces at 5°C/min of S-cPPA, methanol-doped S-cPPA, P-cPPA, and BF₃-doped P-cPPA. (b) Bar chart of onset and endset temperatures for S-cPPA, methanol-doped S-cPPA, P-cPPA, and BF₃-doped P-cPPA during 5°C/min ramp experiments. (c) Dynamic TGA traces at 5°C/min of a P-cPPA film and P-cPPA films doped with TEMPO and DBPDA. (d) Bar chart of onset and endset temperatures from dynamic TGA experiments for P-cPPA, TEMPO-doped P-cPPA, and DBPDA-doped P-cPPA films.

To maximize the thermal stability of the cPPA at elevated temperatures, the effect of TEMPO and DBPDA on the thermal degradation of purified cPPA was investigated. Films were prepared as described above, and the degradation kinetics were measured by TGA. As shown in Figure 8, P-cPPA with and without inhibitors begins to depolymerize at ca. 145°C. Notably, the addition of TEMPO does not significantly affect the degradation behavior of the cPPA, indicating that whatever potential radical pathway was operative in the S-cPPA is no longer a major degradation pathway in P-cPPA. In contrast, addition of DBPDA does not significantly change the depolymerization onset, but does substantially slow the rate of the depolymerization, resulting in the highest endset temperature of any cPPA (187°C). This suggests that an acid-catalyzed, cationic degradation mechanism may still be the operative thermal degradation pathway for P-cPPA at elevated temperatures greater than 140°C. Although beyond the scope of the present study, future work to firmly establish the thermal degradation mechanism of cPPA is warranted.

4.3 Bulk Processing of cPPA

The drastic increase in stability demonstrated herein creates an opportunity to revisit the possible thermal processing of cPPA. Previously, thermal processing was not feasible because S-cPPA degraded at relatively low temperatures. Since the temperature of degradation was well below any glass or melt transitions, it was not possible to use thermal processing techniques without also depolymerizing the cPPA. With the increase in stability provided by better purification procedures and depolymerization inhibitors, we reevaluated the feasibility of thermally processing cPPA. This has several advantages over solvent casting including: minimal residual solvent, more complex architectures with the use of molds, and less waste of toxic solvents. Our strategy was to depress the thermal transitions of cPPA significantly below the temperature of degradation, and facilitate thermal processing in a regime that does not initiate thermal degradation.

4.3.1 Plasticization of cPPA

The thermal transitions of cPPA were depressed by incorporating the plasticizer diethylphthalate (DEP). A plasticized cPPA film was solvent cast from a solution of P-cPPA, 20 phr of DEP, and 3.0 phr of DBPDA in DCM. After solvent evaporation, a free-standing, plasticized, and inhibited cPPA film was recovered. The glass transition temperature of this film was measured by DSC to evaluate the degree of plasticization. It has been shown that neat cPPA does not have a glass transition temperature, while cPPA films cast from DCM have a glass transition temperature greater than 95°C. The glass transition temperature for our DEP-doped film was measured to be 24°C (Figure 9a), confirming significant plasticization of cPPA. The repeatability of the DSC results over three consecutive heat-cool-heat cycles, from -100 – 115°C, confirmed that the glass transition temperature was repeatable and that the polymer is stable to relatively high temperatures (>100°C). This is in contrast to DSC scans of standard cPPA cast from DCM, where the polymer film begins to degrade at temperatures > 100°C.

The viscoelastic behavior of the film was measured by DMA. Consistent with the DSC measurements, the average T_g was measured from the peak of tangent of phase lag ($\tan \delta$) to be 30°C (Figure 9b). The storage modulus of the polymer film was ca. 1 GPa at 22°C, but decreased significantly as the material was heated past its glass transition temperature. At 75°C the storage modulus of the polymer film dropped to 10 MPa – a full two orders of magnitude lower than in the glassy regime. It was difficult to retrieve viscoelastic data at temperatures greater than 75°C due to resolution limits of the instrumentation.

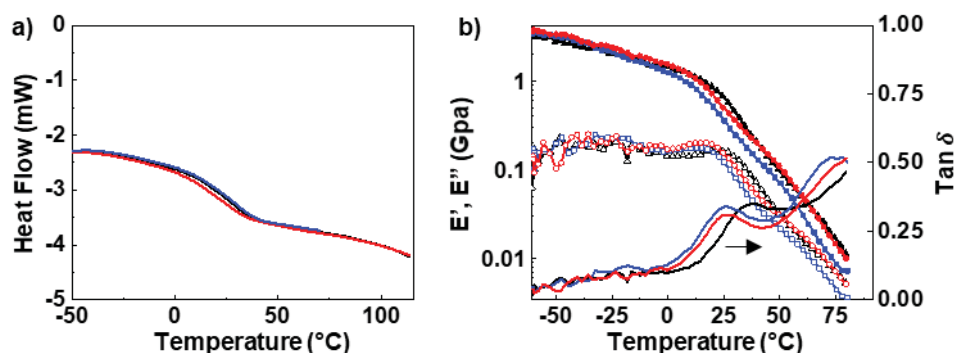


Figure 9: Thermal Transitions of Plasticized cPPA

(a) DSC scans collected at a 20°C/min heating rate and (b) DMA scans collected at a 5°C/min heating rate, showing glass transitions at 24 and 30°C, respectively.

4.3.2 Thermoforming Bulk cPPA

A feedstock of pellets was created from the plasticized cPPA film and then hot pressed in an aluminum mold to create bulk cPPA solid specimens (Figure 10). The pellets were hot pressed at 100°C under an applied pressure of 80 kPa for 15 min. A temperature of 100°C was chosen based on a combination of DMA experimental data and observed behavior of the plasticized cPPA at elevated temperatures, and degradation onsets measured by dynamic TGA experiments. Fifteen minutes under applied pressure was sufficient for the polymer to flow, fill the mold cavity, and produce a uniform disk shape after cooling. The resulting cPPA disk was cut to form pellets for a second round of hot pressing into a triangular mold. Under the same hot press molding conditions, a bulk equilateral triangular piece was successfully molded measuring 2.54 cm on each side and 2.5 mm thick. The molecular weight and NMR spectra were measured for the final triangular specimen to evaluate the effects of two successive thermal processing cycles on the stability of the polymer. The molecular weight measured after this second thermal processing was 136 kDa showing no significant molecular weight decrease. Some monomer was observed by NMR (Figure 6), but a significant amount of polymer remained.

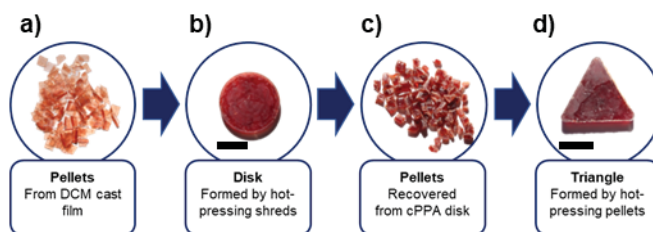


Figure 10: Thermal Processing of cPPA

Procedural schematic of bulk solid formation via cPPA hot press molding. Recyclable cPPA thermoforming process showing: (a) shredded cPPA stock, (b) a hot press molded cPPA disk, (c) cPPA pellets recovered from the cPPA disk, and (d) a hot press molded triangle formed from the recovered cPPA pellets.

4.3.3 Transient Properties of Bulk cPPA

Since the main motivation in the study and application of cPPA is its triggered depolymerization, we investigated how the incorporation of a plasticizer and inhibitor affected its triggered depolymerization response. Figure 11 demonstrates both heat and acid triggering mechanisms. As expected, the addition of trifluoroacetic acid immediately began to depolymerize the bulk cPPA part, resulting in the complete depolymerization of cPPA into *o*PA within 15 min (Figure 11c). Similarly, an elevation in temperature to 150°C degraded the bulk cPPA part within 1 min, resulting in the evaporation of the monomer *o*PA and formation of red residue from the DBPDA (Figure 11d).

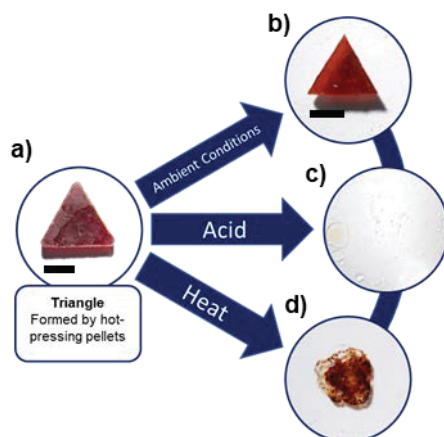


Figure 11: Demonstrated Transience of Monolithic cPPA

Behavior of a monolith cPPA solid (a) under: (b) ambient conditions, (c) exposure to acid, and (d) heat treatment.

These results demonstrate an approach to the thermal processing of a depolymerizable polymer. The multiple cycles of hot press molding confirm that this material can flow at moderate temperatures and under low pressures without undergoing significant thermally-triggered depolymerization. To date, only relatively thin (ca. 400 μm) cPPA films could be successfully produced by solvent casting. We demonstrate the production of 2.5 mm thick bulk cPPA via thermoforming in this paper. This approach overcomes a daunting technical challenge for the processing of cPPA. For the first time, we show the facile manufacture of bulk transient polymer capable of triggered depolymerization.

4.4 Previous Research Directions and Publications

On the path to production of the ultimate deliverable, a bulk transient material, several other research directions were pursued. This work has led to 3 publications, 1 publication in review, and 2 publications pending submission. The publications in print are “Triggered Transience of Metastable Poly(phthalaldehyde) for Transient Electronics”[3], “Tunable Thermal Degradation of Poly(vinyl butyl carbonate sulfone)s via Side-Chain Branching”[1], and “Thermally Triggered Degradation of Transient Electronic Devices”[4]. A publication in review is titled “Cyclic poly(phthalaldehyde): Thermoforming a Bulk Transient Material”. Two publications pending submission are “Processing Dependent Mechanical Properties of Solvent Cast Cyclic

Polyphthalaldehyde” and “Accelerated Thermal Depolymerization of Cyclic Polyphthalaldehyde with a Polymeric Thermoacid Generator”.

4.4.1 Ultraviolet-Triggered Transient Electronics

The work presented in this section is based on the publication “Lopez Hernandez, H.; Kang, S.-K.; Lee, O. P.; Hwang, S.-W.; Kaitz, J. A.; Inci, B.; Park, C. W.; Chung, S.; Sottos, N. R.; Moore, J. S.; Rogers, J. A.; White, S. R.. Triggered Transience of Metastable Poly(phthalaldehyde) for Transient Electronics. *Adv. Mater.* 26 (45), 7637–7642 Copyright © 2014 John Wiley & Sons, Inc.” Previous efforts in transient electronics have relied on device transience initiated by the dissolution of the constitutive materials. This limits the application of these devices because the life-cycle of the system is solely controlled by the dissolution rate of the materials selected at initial fabrication and the reliance on solution based degradation largely eliminates non-biological applications.^[1–4] Metastable polymers, such as those with low ceiling temperatures (T_c), and self-immolative polymers, that can be depolymerized rapidly by specific stimuli (triggers) offer a versatile new avenue for materials selection which provides precise control over the lifetime of the transient device and expands the utility of transient devices beyond dissolution methods alone.^[5–9]

We envision a unique approach towards on-demand physical transience of electronics for a variety of triggering stimuli such as humidity, temperature, or light. These metastable polymers must fulfill several technical criteria: (1) suitably performs as a substrate or encapsulant for microelectronic packaging, (2) depolymerizes in response to an environmental trigger and deactivates the electronics, and (3) allows for tunable degradation kinetics. Among the metastable polymers reported to date, PPA is an ideal candidate for this application due to its low ceiling temperature ($T_c = -43^\circ\text{C}$), easy synthesis with various end-groups, and its rapid depolymerization upon backbone bond cleavage.^[5,10–16] PPA has been used as an acid-degradable photoresist, and its linear, end-functionalized derivatives synthesized by anionic polymerization have been shown to depolymerize selectively in the presence of chemical triggers.^[6,16–20]

In this work, the rapid depolymerization of cPPA with a photoacid generator (PAG) was investigated. Task #2a, #4a, #4b, and #4d from the statement of work are dressed in this work, leading to the development of a polymeric system that depolymerizes when exposed to ultraviolet (UV) light and was used for electronic substrates and packaging with sufficient mechanical properties for easy handling. PAG was used to generate acid in response to irradiation to UV light, which, in turn, begins to cleave the polymer backbone of cPPA and leads to the unzipping depolymerization of cPPA into the monomer oPA. Photo-triggerable transient electronics were fabricated on a cPPA substrate with a PAG additive. The electronics were destroyed by triggering the PAG/cPPA substrates with UV light, and the transient behavior and kinetics were characterized with dynamic mechanical analysis and Fourier transform infrared spectroscopy. Transience rates were tuned by modifying the PAG concentration and the irradiance of the UV source. In addition, we demonstrate the encapsulation of a passive device with PAG/PPA. The degradation of the encapsulating film leads to the degradation of the electrode causing an altered performance of the device. We suggest this can be used as a partial triggering technique where only part of a device is destroyed.

4.4.2 Thermally-Triggered Acid-Wax Emulsions for Transient Electronics

The work presented in this section is based on the publication “C.W. Park, S.-K. Kang, H. Lopez Hernandez, J.A. Kaitz, D.S. Wie, J. Shin, O.P. Lee, N.R. Sottos, J.S. Moore, J.A. Rogers, S.R. White, Thermally Triggered Degradation of Transient Electronic Devices, *Adv. Mater.* 27 (2015).” We report on a materials system that incorporates acid wax emulsions for the destruction of electronic devices, and demonstrate that when coupled with the acid sensitive poly(phthalaldehyde) a fully degradable system can be achieved and addresses tasks #2a, #4a, #4b, and #4d from the statement of work. This work explores easier device fabrication, faster device destruction, and expand the types of triggering modes for transience.

Among various stimuli-responsive systems, heat triggers have been widely studied with thermo-sensitive materials including phase-change and volume-change materials for drug delivery, membranes, and battery shutdown. Notably, the thermal activation can be coupled with other triggering modes such as light, magnetic, or radio frequency (RF) for noncontact heating based on photothermal nanomaterials or induction heating.

Our approach involves the use of thermal-triggered transient electronics based on protective wax coatings that contain encapsulated acid microdroplets. Upon exposure to sufficient heat, the melting of the wax releases the encapsulated acid which then enables rapid device destruction via acidic degradation of electronic components with or without cPPA substrate disintegration. Inert and hard silicone waxes with rapid phase changes above their melting point were selected for coating materials. Sequestration and encapsulation of methanesulfonic acid (MSA) were achieved by melt casting of an acid/wax emulsion. Melting of the wax releases the acid and device destruction follows rapidly. Along with the degradation of Mg traces by MSA, Si-based devices are also destroyed by acid-triggered depolymerization of the cPPA substrate.

4.4.3 Thermally-Triggered Poly(vinyl *t*-butyl carbonate sulfone) Acid Generators and Their Use in the Depolymerizations of cPPA

The work presented in this section is based on paper that will be submitted soon “Lopez Hernandez, H., Lee, O.P., Possanza, C., Kaitz, J.A., Park, C-W., Plantz, C.L., Sottos, N.R., Moore, J.S., White S.R., Accelerated Thermal Depolymerization of Cyclic Polyphthalaldehyde with a Polymeric Thermoacid Generator. *Submission Pending*.” In this chapter, we investigated the incorporation of a poly(vinyl *t*-butyl carbonate sulfone) (PVtBCS) thermoacid generator (TAG) into cPPA films to lower the degradation temperature and accelerate the depolymerization kinetics. It addresses tasks #2a, #4a, #4b, and #4d from the statement of work. The material formulation is processable into free standing films and triggerable when exposed to moderate elevations in temperature ($> 85^{\circ}\text{C}$) and the depolymerization kinetics were investigated.

When cPPA is exposed to acid, protonation results in the cleavage of the acetal backbone, which destabilizes the polymer and initiates an unzipping reaction along the polymer chain.^{3,9,19} Stimuli-responsive acid generating moieties can be used to trigger the depolymerization of cPPA in response to a variety triggers. Heat activates the TAG, which in turn generates acid that catalyzes the cleavage of the acetal bonds in the polymer backbone. Upon cleavage of the acetal bond, the polymer backbone unzips into the *o*PA monomer. At sufficiently high temperatures

(>85°C) the *o*PA monomer will evaporate, leaving < 2 wt% residue after thermal triggering. The activation temperature of the TAG is critical because it defines the triggering temperature for initiating the destabilization and depolymerization of cPPA. Here, we report the acid generating properties of PVtBCS and the manufacture of transient polymeric films with lower activation temperatures and faster degradation kinetics than those of neat cPPA and other polymers reported to date.

A thermally depolymerizable polymer blend made from the thermoacid generator PVtBCS and cPPA was developed. PVtBCS depolymerizes when heated at 85°C to form acidic and volatile byproducts. PVtBCS was blended with cPPA, an acid sensitive polymer with a low ceiling temperature (-42°C), at 0.5, 1.0, and 2.0 wt%. PVtBCS/cPPA films depolymerize into products that evaporate within 80 min at 85°C leaving < 2 wt% of residue. An increase in the thermoacid generator concentration greatly increased the rate of depolymerization for the PVtBCS/cPPA blended films. Molecular weight measurements reveal that an increase in the thermoacid generator concentration greatly increases the rate of depolymerization for the PVtBCS/cPPA blended films with full depolymerization of 2 wt% PVtBCS/cPPA films within 15 min. DMA confirms that all mechanical integrity for 2 wt% PVtBCS/cPPA films is rapidly lost at 85°C. Two different time scales were identified, where one is the time needed for the polymer to depolymerize and the second is the time needed for evaporation of the depolymerization product and ultimately for the ‘vanishing’ of the polymer film.

4.4.4 Poly(olefin sulfone)s

The work presented in this section is based on the publication “Lee, O. P.; Lopez Hernandez, H.; Moore, J. S. ACS Macro Lett. 2015, 4 (7), 665–668.” This section details an investigation into various substituent side chain groups and its effect on the rate of thermal depolymerization.²⁰ This addresses the tasks #1a, #2a, #3a, and #4d.

Polymeric materials that depolymerize into volatiles on command may function as vanishing substrates or packaging for transient electronics. Poly(vinyl tert-butyl carbonate sulfone) is known to afford low-boiling byproducts upon heat-activated degradation; however, the polymer is rather unstable, even to the degree of being difficult to process and handle. Understanding the origin of this instability is important for the development of robust materials capable of programmed self-destruction. In this work, we show that poly(vinyl tert-butyl carbonate sulfone)s thermally decompose via carbonate elimination as the rate-determining step, indicating that its thermal instability stems from the lability of the tert-butyl carbonate group. We further examined the effect of isomeric butyl carbonate side chains on the thermal degradation of poly(vinyl butyl carbonate sulfone)s and found that the degradation onsets range from 91 to 213°C, yielding as little as 2.77 ± 0.53 wt % residue. Results from our findings will aid in the development of vanishing polymers with tunable thermal degradation.

In summary, preliminary mechanistic studies show that poly(vinyl butyl carbonate sulfone)s thermally decompose via carbonate elimination as the rate-determining step. We used these results to guide polymer design; by modulating side-chain substitutions, we demonstrate control over thermal depolymerization of these polymers. Consistent with the proposed mechanism, *t*-butyl (P1), *s*-butyl (P2), *i*-butyl (P3), and *n*-butyl (P4) exhibit increasing thermal stability with decreasing side-chain branching at the β -carbon to the carbonyl group. Thermally triggering the

depolymerization of P1, P3, and P4 affords little solid residue, a characteristic that is desirable for the development of transient materials. Mechanical characterization of the polymers reveals that films of P2 and P4 are more easily manipulated than those of P1 and P3. We further show the complete physical transience of a film fabricated from P1, which rapidly vanishes at 110°C within 12 min. The design and synthesis of these thermally degradable poly(olefin sulfone)s represent the first step toward developing transient substrates and packaging.

4.4.5 Unproductive Research Directions

The original statement of work included multiple research directions which were considered unproductive or low priority. Notable research directions that were pursued include mechanically robust, base-sensitive polymers; flash-triggering by acid amplification; and frontal depolymerization. The initial results from each of these unproductive research directions is discussed below.

4.4.5.1 Mechanically Robust Base-Sensitive Polymers

Poly(olefin sulfone)s were investigated as potential base-sensitive polymers that would depolymerize into volatile byproducts in response to exposure to base. We demonstrated that these polymers thermally depolymerize at elevated temperatures $> 75^{\circ}\text{C}$ and that the triggering temperature is tunable with modification of the side chain branching.²⁰ Poly(olefin sulfone)s also depolymerize readily upon exposure to base because of the strong electron withdrawing sulfonyl group that makes the protons on the neighboring carbon easily abstracted by bases, leading to a chain reaction that depolymerizes the polymer into the olefin monomer and sulfur dioxide.^{20,21} However, the stability of poly(vinyl t-butyl carbonate sulfone) was too low to yield mechanically robust materials due to room temperature depolymerization. Other poly(olefin sulfones) or poly(vinyl ether sulfone)s were synthesized, but the triggering and mechanical properties were not quantified. This is an area of possible future exploration.

4.4.5.2 Flash-Triggering by Acid Amplification

Flash triggering of cPPA by acid amplifiers was tested with no success. The addition of an acid amplifier resulted in premature depolymerization of the cPPA because of the autocatalytic effects of the acid amplifier and the high acid sensitivity of cPPA. Since a single acid cleavage of the cPPA backbone results in complete unzipping, very small concentrations of residual acid may result in premature depolymerization of the entire polymer. Residual acid also triggers the acid amplifier which results in the accelerated generation of acid resulting in elevated concentrations of acid that accelerate the depolymerization of cPPA. Further exploration in this space would require an extremely stable acid amplifier and careful purification procedures to remove residual acid products that can initiate the acid generation reaction prematurely.

4.4.5.3 Frontal Depolymerization

Frontal depolymerization is a self-propagating depolymerization reaction that requires an initial energy input ‘trigger’ at a single location to depolymerize the entire polymer. We were interested in frontal depolymerization because triggering at only a localized region would reduce the required energy input and remove the need to trigger the entire polymer (which may be difficult in application). In frontal polymerization, an exothermic polymerization reaction becomes self-

propagating because the energy of reaction generates enough heat to polymerize neighboring monomer resulting in a continual polymerization front. In a similar fashion, we believe that frontal depolymerization may propagate due to increased reactivity at the depolymerization front. The exact mechanism for the increased reactivity is unknown, but we hypothesize that increased dissolution from monomer formation and increased local concentration of acid from acid generators may contribute to faster depolymerization rates at the point of triggering.

Frontal depolymerization was tested with 2 wt% PVtCBS, as an acid generator, mixed with cPPA and neat cPPA. Frontal depolymerization was evaluated at both room temperature and 85°C by triggering depolymerization in a small region with a localized heat source. At room temperature the depolymerization did not continue for either the PVtCBS doped or neat cPPA film and no depolymerization front was observed for 24 h. However, at 85°C the depolymerization continued from the point of triggering resulting in a more rapid depolymerization over a sample at 85°C with no localized triggering. Importantly, a neat sample at 85°C will depolymerize over very long times (> 4 h), yet the locally triggered cPPA depolymerized completely within 30 min. It appears that locally initiating the depolymerization of cPPA a priori overcomes the initiation barrier required for thermal depolymerization of cPPA, resulting in a depolymerization front starting from the point of localized initiation. The propagation reaction is negligibly slow at room temperature, but can be accelerated to acceptable rates at around 85°C.

This result demonstrates that the triggering of cPPA depolymerization would benefit from a large ‘burst’ of thermal energy to a localized region that guarantees immediate localized depolymerization. After initial triggering, a more moderate temperature profile that maintains an acceptable propagation rate should be maintained.

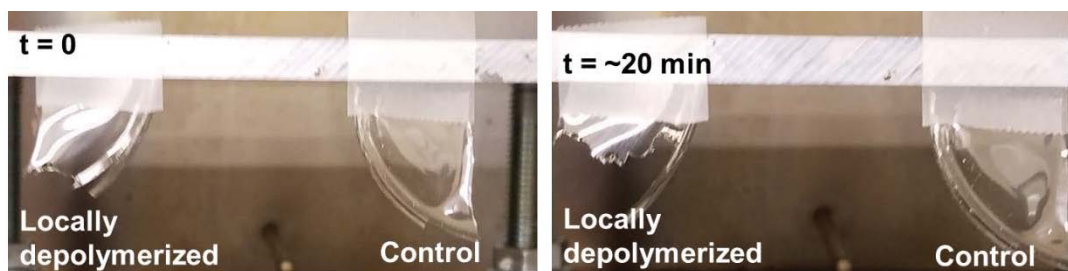


Figure 12: Frontal Depolymerization of a Locally Depolymerized Neat cPPA film at 105°C
No thermal depolymerization of the control film was observed while the locally polymerized film frontally depolymerizes from the point of triggering.

4.5 Commercialization of cPPA

cPPA recently became commercially available, sold by Sigma Aldrich, and produced using the procedures developed by Kaitz, et al. under this research. Sigma sells a stock of cPPA at a cost of 196.00 USD per 500 mg vial (catalog # 809144). We obtained a sample of this product, and analyzed the chemical properties. Our analysis is discussed below.

4.5.1 Molecular Properties

Samples of cPPA obtained from Sigma Aldrich were analyzed by both GPC and ^1H NMR. The GPC analysis is shown in Figure 13. No elution peaks corresponding to polymer or even oligomer were observed. Surprisingly, the only peaks observed by GPC correspond to small molecules.

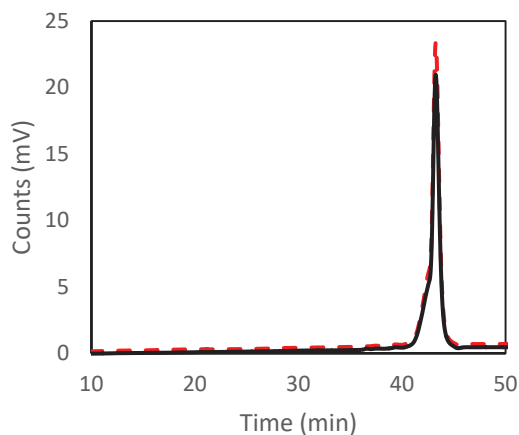


Figure 13: GPC Analysis of cPPA Obtained from Sigma Aldrich

GPC traces of the cPPA purchased from Sigma Aldrich, showing only small molecule peak during two duplicate analyses.

To further characterize the material obtained from Sigma Aldrich, proton NMR spectra were acquired. Shown below in Figure 14 is one such spectrum. Importantly, no resonances were observed for the cPPA polymer, and the only observable resonances were those of the monomer, *o*PA. Troublingly, it appears that the samples obtained from Sigma Aldrich were exclusively *o*PA, and contained no polymer whatever. They appear to have not yet discovered appropriate measures to stabilize the polymer i.e., the measures that we have discovered and detailed in Section 4.2 of this report.

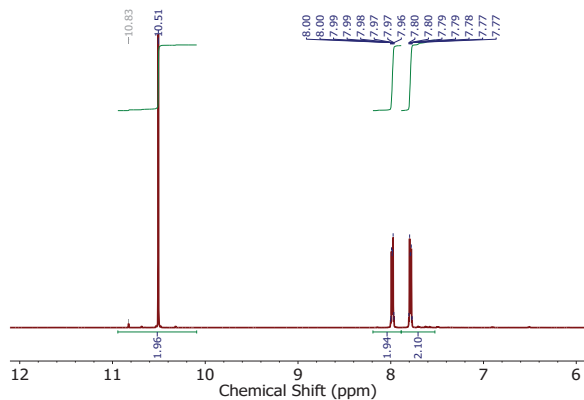


Figure 14: NMR Analysis of cPPA Obtained from Sigma Aldrich

*^1H NMR spectrum of cPPA purchased from Sigma Aldrich, showing only resonances corresponding to the monomer, *o*PA.*

4.5.2 Stability and Utility in Transient Materials Applications

Under the hypothesis that any polymer present in the material obtained from Sigma Aldrich may have degraded before analyses were complete (which was unlikely, as cPPA is indefinitely stable in THF), the material was subjected to the enhanced purification protocol described earlier in this report. However, upon attempted precipitation of a DCM solution containing the material into methanol, no precipitate was formed. That the material was completely soluble in methanol is consistent with the purchased material being entirely composed of monomer. Since the material contained no polymer, we were unable to evaluate the stability or application to previously described systems.

At this juncture, it appears that there is not reliable commercial source of cPPA. We will be contacting Sigma Aldrich in the near future to discuss improved techniques for the production and distribution of cPPA, in the hopes that we may aid in the commercialization of this transient polymer.

5 CONCLUSIONS

We presented tools for tailoring the thermal degradation behavior cPPA and leveraging that control to enable thermal processing and molding in bulk quantities. Based on the proposed radical and cationic depolymerization mechanisms, TEMPO and DBPDA were added to inhibit the depolymerization of cPPA. Both TEMPO and DBPDA significantly increased the degradation onset temperature for cPPA. We also discovered that the concentration of residual BF_3 could be significantly decreased by precipitating the polymer in 15 μL droplets, which resulted in a drastic increase of the degradation onset temperature. cPPA, plasticized with DEP and stabilized with DBPDA, was hot press molded twice at 100°C into bulk specimens that maintained both heat and acid triggered depolymerization functionality. This is the first demonstration of a bulk polymer solid with the capability of triggered depolymerization. In the future, this approach may enable the formation of more complex architectures fabricated from a triggerable polymer for engineering applications.

6 REFERENCES

- (1) Aso, C.; Tagami, S. *Macromolecules* **1969**, 2, 414.
- (2) Aso, C.; Tagami, S.; Kunitake, T. *Journal of Polymer Science Part A-1: Polymer Chemistry* **1969**, 7, 497.
- (3) Hernandez, H. L.; Kang, S.-K.; Lee, O. P.; Hwang, S.-W.; Kaitz, J. A.; Inci, B.; Park, C. W.; Chung, S.; Sottos, N. R.; Moore, J. S.; Rogers, J. A.; White, S. R. *Advanced Materials* **2014**, 26, 7637.
- (4) Ito, H.; Willson, C. G. *Polymer Engineering & Science* **1983**, 23, 1012.
- (5) Ito, H.; England, W. P.; Ueda, M. *Journal of Photopolymer Science and Technology* **1990**, 3, 219.
- (6) Phillips, O.; Schwartz, J. M.; Engler, A.; Gourdin, G.; Kohl, P. A. In *2017 IEEE 67th Electronic Components and Technology Conference (ECTC)* 2017, p 772.
- (7) Gourdin, G.; Phillips, O.; Schwartz, J.; Engler, A.; Kohl, P. In *2017 IEEE 67th Electronic Components and Technology Conference (ECTC)* 2017, p 190.
- (8) Kaitz, J. A.; Diesendruck, C. E.; Moore, J. S. *Journal of the American Chemical Society* **2013**, 135, 12755.
- (9) Park, C. W.; Kang, S.-K.; Hernandez, H. L.; Kaitz, J. A.; Wie, D. S.; Shin, J.; Lee, O. P.; Sottos, N. R.; Moore, J. S.; Rogers, J. A.; White, S. R. *Advanced Materials* **2015**, 27, 3783.
- (10) Diesendruck, C. E.; Peterson, G. I.; Kulik, H. J.; Kaitz, J. A.; Mar, B. D.; May, P. A.; White, S. R.; Martínez, T. J.; Boydston, A. J.; Moore, J. S. *Nature Chemistry* **2014**, 6, 623.
- (11) Ito, H.; Schwalm, R. *Journal of The Electrochemical Society* **1989**, 136, 241.
- (12) Köstler, S.; Zechner, B.; Trathnigg, B.; Fasl, H.; Kern, W.; Ribitsch, V. *Journal of Polymer Science Part A: Polymer Chemistry* **2009**, 47, 1499.
- (13) Seo, W.; Phillips, S. T. *Journal of the American Chemical Society* **2010**, 132, 9234.
- (14) DiLauro, A. M.; Robbins, J. S.; Phillips, S. T. *Macromolecules* **2013**, 46, 2963.
- (15) Ito, H.; Ueda, M.; Schwalm, R. *Journal of Vacuum Science & Technology B: Microelectronics Processing and Phenomena* **1988**, 6, 2259.
- (16) Steinmann, A. In *Santa Clara Symposium on Microlithography*; SPIE: 1988; Vol. 0920, p 8.
- (17) Kaitz, J. A.; Moore, J. S. *Macromolecules* **2014**, 47, 5509.
- (18) Schwartz, J. M.; Phillips, O.; Engler, A.; Sutlief, A.; Lee, J.; Kohl, P. A. *Journal of Polymer Science Part A: Polymer Chemistry* **2017**, 55, 1166.
- (19) Tsuda, M.; Hata, M.; Nishida, R. I. E.; Oikawa, S. *Journal of Photopolymer Science and Technology* **1993**, 6, 491.
- (20) Lee, O. P.; Lopez Hernandez, H.; Moore, J. S. *ACS Macro Letters* **2015**, 4, 665.
- (21) Possanza Casey, C. M.; Moore, J. S. *ACS Macro Letters* **2016**, 5, 1257.

LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS

ACRONYM	DESCRIPTION
°C	Degrees Celsius
μL	Microliters
μm	Micrometers
μmol	Micromoles
BF ₃	Boron Trifluoride
cPPA	cyclic Poly(Phthalaldehyde)
Da	Daltons
DBPDA	<i>N,N'</i> -di- <i>sec</i> -butyl-1,4-phenylenediamine
DCM	Dichloromethane
DEP	Diethylphthalate
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
E'	Storage Modulus
E''	Loss Modulus
F	Fluorine
g	Grams
GPa	Gigapascals
GPC	Gel Permeation Chromatography
h	Hours
H	Hydrogen
HPLC	High-Performance Liquid Chromatography
Hz	Hertz
kDa	Kilodaltons
kPa	Kilopascals
mg	Milligrams
MHz	Megahertz
min	Minutes
mL	Milliliters
mm	Millimeters
M _n	Number Average Molecular Weight
MR	Repeat Unit Molecular Weight
MSA	Methanesulfonic Acid
mW	Milliwatts
M _w	Weight Average Molecular Weight
MW	Molecular Weight
NMR	Nuclear Magnetic Resonance
<i>o</i> PA	<i>ortho</i> -Phthalaldehyde
PAG	Photoacid Generator
P-cPPA	Purified cyclic Poly(Phthalaldehyde)
PDI	Polydispersity Index
phr	Parts per hundred rubber
PPA	Poly(Phthalaldehyde)
ppm	Parts per million

ACRONYM	DESCRIPTION
PTFE	Poly(Tetrafluoroethylene)
PVtBCS	Poly(Vinyl <i>t</i> -Butyl Carbonate Sulfone)
RF	Radio Frequency
S-cPPA	Standard process cyclic poly(phthalaldehyde)
TAG	Thermoacid Generator
Tan δ	Tangent of phase lag
T _c	Ceiling Temperature
TEMPO	(2,2,6,6-Tetramethylpiperidin-1-yl)Oxyl
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
UV	Ultraviolet
wt%	Weight percent